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Heterogeneous catalysts for production of chemicals using carbon dioxide as raw material: A review

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ABSTRACT

The utilization of CO_2 for the production of useful chemicals using heterogeneous catalysts is one of the ways to reduce the anthropogenic greenhouse gases in the atmosphere. In many cases, the CO_2 conversion and products yield are still considered very low and need to be operated at high pressure and temperature. The critical point in CO_2 conversion is to activate the CO_2 molecules either by adding a co-reactant or by using effective catalysts. This paper presents the current development on the effect of several precursors like metals, metal oxides, ionic liquids, and acid–base loaded on a suitable support in creating magical properties of catalysts on the performance of CO_2 conversion. Cu/ZnO-based catalysts, ionic liquid-based catalysts, and metal oxides-based catalysts are reported to be the most effective catalysts in the formation of methanol, cyclic carbonates and dimethyl carbonate. This review also focuses on various strategies and developments in altering heterogeneous catalysts, followed by critical factors of CO_2 molecule activation, and the optimization of the catalytic activity or catalysts reusability.

Contents

1. Introduction

CO_2 is an abundant carbon source and one of the major greenhouse gases, which is produced from chemical industry, energy

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supply industry, power plant and transportation sector that use fossil fuels as their resources [1–4]. CO_2 is also an abundant natural feedstock which is relatively cheap and non-toxic [5–8]. The enormous discharge of CO_2 is not only degrading the resources but also polluting the environment, causing the global warming effect. There are four pathways in cutting the carbon emission, which are (i) reduce energy consumption by improving efficiency, (ii) switch of fossil fuels with carbon neutral or renewable energy sources, (iii) capture and storage of CO_2 chemically, physically or biologically, and (v) convert CO_2 to various useful chemicals. The scope of this review is restricted only to the utilization of CO_2 to produce useful chemical products.

Furthermore, high stability, inert property and lower reactivity of CO_2 molecule in various chemical reactions are probably the major reasons why this compound is not widely used in the industry. Thermodynamically stable CO_2 molecule, substantial energy input, active catalysts, and optimum reaction conditions are necessary for successful CO_2 conversion [5,7,9,10]. The detail plotting data for thermodynamic CO_2 conversion involving CO_2 Gibbs free energy and related co-reactants has been reported by Song [10].

CO_2 has been used in the production of chemicals or intermediates such as methanol, cyclic carbonates, and dimethyl carbonate for chemical industry usage via CO_2 hydrogenation, CO_2 cycloaddition to epoxides and CO_2 with acetals, or ortho-ester, or methanol with or without epoxides, respectively. A substantial amount of research has been done on chemical reactions converting CO_2 to useful chemicals over the homogeneous and heterogeneous catalysts. Both homogeneous and heterogeneous catalysts have their own advantages and disadvantages. Homogenous catalytic system typically has higher catalytic activity than heterogeneous catalyst counterparts. However, heterogeneous catalysts are preferable due to the simplicity in reactor design, separation, handling, stability and reusability of catalyst [5,11]. The high efficiency of heterogeneous catalyst employed could reduce the production cost especially for large-scale industrial processes [11]. The challenge in combining unique homogeneous catalysts properties with special heterogeneous catalysts technical part, to create magical catalysts properties became the significant direction in a recent study. This facilitates an interesting challenge and opportunities in exploring and developing new concepts and technologies for chemical industries and research areas worldwide [4]. This review presents an overview on the potential of heterogeneous catalysis on CO_2 utilization in synthesis of methanol, cyclic carbonate and dimethyl carbonate. The focus is on the heterogeneous catalysts properties, CO_2 conversion, products yield, reaction conditions, limitation, and reaction mechanism.

2. Synthesis of methanol

Catalytic synthesis of methanol directly from CO_2 and H_2 holds as a central technology to solve the CO_2 problem. Methanol can be considered as a starting feedstock in chemical industries and as an alternative to fossil fuels [9,12–14]. On industrial scale, methanol is currently produced from syngas by employing metal based catalysts. Replacing of CO with CO_2 in methanol synthesis is a great challenge in CO_2 utilization. Methanol synthesis from atmospheric CO_2 and hydrogen is considered as one of the economic ways to alleviate the global warming and to drive chemical and energy companies towards a more sustainable use of resources [5,9].

2.1. Limitation in methanol formation

In CO_2 hydrogenation to methanol processes, the reaction part can be represented as follows [5,13,15]:Methanol formation

$$CO_2 + 3H_2 \rightarrow CH_3OH + H_2O \qquad (1)$$

Reverse water–gas-shift reaction (RWGS)

$$CO_2 + H_2 \rightarrow CO + H_2O \qquad (2)$$

The formation of methanol increases with the decrease of reaction temperature and increase of pressure due to the exothermal CO_2 and H_2 reaction, endothermic RWGS reaction and reduction of reaction molecule number [5,9,16,17]. Moreover, the high reaction temperature favours the formation of undesired by-products such as higher alcohols and hydrocarbons, which reduces the methanol selectivity [12,13]. The low reactivity and chemically inert CO_2 require a reaction temperature more than 240 °C to activate the CO_2 molecules to produce methanol [5,9,13]. In CO_2 hydrogenation, the medium activation energies are decisively lower for the methanol formation than those of the RWGS reaction. The large amount of water that comes from both the reactions acts as inhibitors on the active sites, leading to the deactivation of catalyst and subsequently reducing the consecutive step in the production of methanol [5,9,16].

Highly efficient catalysts properties are the major factor in CO_2 molecules activation to increase methanol production and avoid by-products formation. The catalysts used in CO_2 hydrogenation were mostly modified from CO hydrogenation catalysts. To date, an efficient catalyst to activate the CO_2 molecule has not been fully exploited for industrial applications due to the lack of design and technology in controlling the catalyst properties together and understanding the reaction mechanism. The heterogeneous catalytic activity of CO_2 hydrogenation to methanol depends on various factors: (i) the metal and catalyst structures; (ii) the uniform particle size of the metal; (iii) the distribution of metal on the support; (iv) the surface area of catalysts; (v) the active sites on catalyst; (vi) the stability and long-term operation; (vii) the types of promoters and supporters and (viii) the growth of the metal particle [4,5,12–14,16–19].

2.2. Reaction mechanism

The mechanism of CO_2 hydrogenation to methanol over Cu/ZnO catalyst using ab initio molecular orbital (MO) calculation was proposed by Kakumoto and Watanabe [20], as shown in Fig. 1. The CO_2 is adsorbed on the Cu^+ site. The H atom from H_2 is being adsorbed on the metallic Cu and then attacking the C atom in adsorbed CO_2, subsequently forms the formate intermediate [20,21]. Then, the C–O bond is broken simultaneously when H atoms attack the formate species on the C and O atoms, which then generates formaldehyde intermediate on the Cu^+ site. The heterogeneous dissociation of H_2 adsorbed on ZnO generates H^- on the Zn sites and attacks the C atom of the formaldehyde to form the intermediate methoxy. Finally, methanol is produced when the H^+ on the O atom of ZnO attacks the O atom of the methoxide [20]. The presence of Cu^+ species in the catalyst led to higher methanol selectivity and lower RWGS reaction [13]. However, no promotional effect of Zn has been found for the RWGS reaction producing carbon monoxide and water [17,20].

Furthermore, the post-reaction surface analysis measured by XPS which was studied by Fujitani et al. [17] demonstrated that the formate species formation occurred on the Cu surface as an intermediate reaction during methanol formation. The formate coverage linearly increased with the Zn coverage below θ_{zn}=0.15, indicating that the formate species formation was stabilized by the Zn species [17]. At higher Zn coverage, more Zn was readily oxidized on Cu to ZnO during the reaction of hydrogenation, while Zn was partially oxidized without oxygen to ZnO or O on the surface of Cu under the reaction conditions. Thus, the Zn on Cu species was directly bound to the oxygen of the surface formate species as the active sites [17]. However, the mode of the copper

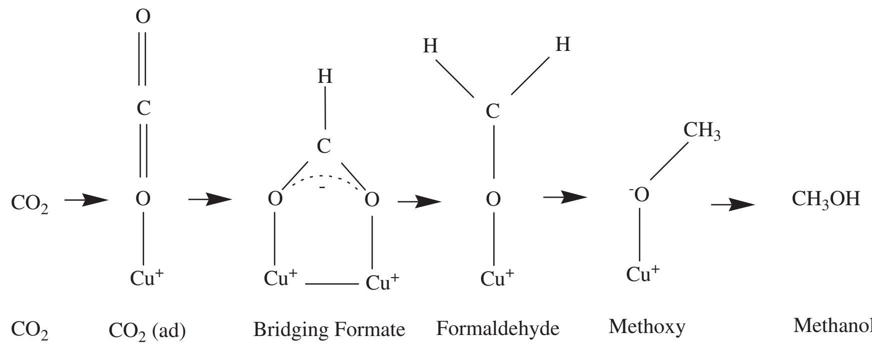


Fig. 1. CO_2 hydrogenation mechanism on Cu/ZnO catalyst proposed by ab initio MO calculations [20].

presence on the surface and its interaction with the promoters are also crucial for optimizing the methanol formation [12,13].

2.3. Catalytic performance

2.3.1. Cu/ZnO catalysts

Over the past few decades, Cu/ZnO catalyst has been intensively studied for CO_2 hydrogenation to methanol [20,22–24]. Copper alone is not efficient in the synthesis of methanol from CO_2 [12,13]. The preparation of Cu/ZnO catalyst by physical mixture of Cu/SiO_2 and ZnO/SiO_2 resulted in formation of the ZnO_x on the surface of Cu particles to stabilize Cu^+, which is a crucial catalytic species. Higher ZnO/SiO_2 content gives a remarkable performance three times greater than that of Cu/SiO_2 due to the role of ZnO/SiO_2 in creating Cu^+ and Cu^0 as active species in driving the hydrogenation steps for the production of methanol [17,23]. Moreover, the mixture was beneficial for stabilization of Cu^+ sites on the Cu surface as ZnO could control the Cu^+/Cu^0 ratio without affecting the Cu morphology [21,23]. Toyir et al. [13] and Choi et al. [21] proposed that the ZnO acts as a support and a dispersing agent during the impregnation process. For Cu/ZnO catalyst, the hydrogen was reported to come from the spillover of copper and subsequently involved in methanol synthesis on the supports [13].

2.3.2. Multicomponent catalysts

Although Cu/ZnO catalyst has been reported to be an active catalyst for methanol formation, the presence of well-dispersed Zn alone cannot guarantee a strong junction connecting the active species of Cu [16]. Therefore, various CO_2 hydrogenation catalysts containing both Cu and Zn metal as the main components with different modifiers have been developed. The metal surface areas and dispersion are generally observed to be one of the main active sites in CO_2 hydrogenation over multicomponent catalysts [12,13,16,19]. The addition of Ga_2O_3 on Cu/ZnO has a good promoting effect towards the methanol production, which achieved two times higher methanol selectivity than the respective Cu/ZnO due to the interaction at atomic scale between the metal oxide and copper, and strong promoting effect of Ga_2O_3 species on the catalyst activity and stability [13]. The loading of gallium-promoted copper-based catalysts onto Si and ZnO supports by impregnation and co-impregnation of methoxide was reported by Toyir et al. [12,13]. The use of hydrophobic silica supported catalyst could give higher surface area, pore volume and stability than that of ZnO, which could enhance the conversion and selectivity at the temperatures up to 270 °C due to the hydrophobic silica support led in highest dispersion of Ga_2O_3 and a better interaction between ZnO, Ga_2O_3 and Cu active sites [12,13].

Toyir et al. [16] studied two categories of metal oxides which are effective in catalyst synthesis. Al_2O_3 or ZrO_2 added on Cu/ZnO could increase the surface area and Cu particles dispersion, while Ga_2O_3 or Cr_2O_3 could increase the activity per unit copper surface area of the catalyst [12,13,16]. Small amount of silica added on the catalyst greatly enhanced the catalyst stability up to 500 h by suppressing the metal crystallization due to the suppressing agglomeration of Cu and ZnO metal by silica, which partially covered the surface of metal particles in the catalyst during the initial deactivation [16,25]. Sloczynksi et al. [26] reported that Au and Cu had a similar and better distribution than Ag and their surface areas decreased when the metal contents increased. In the case of Cu and Au, the addition of large amounts of CuO and AuO led to the formation of large pore diameter of catalysts in contrast with Ag loading [26]. This could be attributed to the formation of large Ag crystallites that eliminate the porous structure of catalyst. However, the introduction of Cu exhibited higher catalytic activity than the catalyst containing Ag and Au because of the synergy effect between the Cu and ZnO or ZrO_2 [26]. The presence of Cu^+ favours the hydrogenation of CO_2 due to the strong stabilization effect of Cu^+ ions on the surface of ZnO or/and ZrO_2 supports compared to the catalyst containing Ag^+ and Au^+ ions, which becomes unstable at the reaction temperature [26]. In contrast to the transition metal, metallic Cu or metal on group IB showed an exceptional activity because of their low ability in activating the dissociative adsorption process of hydrogen. The dissociation adsorption of hydrogen on those metals is located on a support [26]. Noble metals have ideal low-index, large crystal size which also did not form an enduring bonding with atomic hydrogen [26]. The addition of vanadium could enhance the dispersion of supported CuO species and form a new phase over Cu–V binary oxide supported on γ-Al_2O_3 catalyst to assist the hydrogenation of CO_2 [15].

Sloczynski et al. [27] studied the effect of various metal oxides added to $Cu/ZnO/ZrO_2$ catalyst for CO_2 hydrogenation to methanol. They observed that the catalyst synthesized by co-precipitation of mixed carbonates for $Cu/ZnO/ZrO_2$ catalyst gave small CuO crystallites compared to the catalyst prepared by complexing with citric acid. This is due to the fundamental mechanism, in which the size of CuO crystallites has already been generated during the precipitation stage. Thereafter, the growth of CuO crystallites is hindered during the calcination stage according to the separation space between ZnO and ZrO_2 particles. On the other hand, the unlimited growth of CuO crystallites via complexing citric acid formed during the calcination, reduction and operation steps in the reactor, results in larger crystallites growing at the expenditure of the smaller ones. The presence of small crystallites of metal is considered due to their role in metal dispersed phase stabilization on the surface of the supporter [27]. Similarly Toyir et al. [13] reported that when Ga_2O_3 was added to metal based catalyst MnO and B_2O_3 addition was found to improve the initial CuO dispersion during the synthesis of catalyst, however it underwent the CuO sintering during the reaction run. The intermediate properties are shown by the addition of Y and Gd, and a very

negative dispersion effect on both the Cu and CuO is presented by In metal [27]. The H-reduction of $YBA_2Cu_3O_7$ at 250 °C was favorable in the synthesis of methanol because of orthorhombic to tetragonal structure of $YBA_2Cu_3O_7$ catalyst [28]. In tetragonal $YBA_2Cu_3O_7$, only Cu^{2+} and Cu^{+} exist with no metallic Cu^0. During the H-reduction of $YBA_2Cu_3O_7$, there were oxygen vacancies, which act as a platform for electron trap in the reoxidation of existed Cu^{+} to Cu^{2+}. The redox between the Cu^{+} to Cu^{2+} might play an important role in methanol synthesis from CO_2 hydrogenation [28].

The improved catalyst structural properties via reverse co-precipitation under ultrasound irradiation have been proposed by Arena et al. [29]. High dispersion of Cu–ZnO/ZrO_2 catalyst with large surface area and exposure to active Cu phase was successfully synthesized. By reverse co-precipitation method, simultaneous precipitation of Cu^{2+}, Zn^{2+} and ZrO^{2+} cations that act as active sites can be obtained through a slow dropwise addition of the precursor solution to the precipitating agent. The texture, morphology and reactivity of the catalysts were found to be influenced by the irradiation energy of ultrasound during catalyst preparation [29]. In the further study, an intimate mixing of nanosized oxide during synthesis of the Cu/ZnO/ZrO_2 was found to be dominant in hindering the formation of controlled crystalline phase to obtain good metal nanoparticles dispersion on the catalysts surface [30]. The strong Cu metal interaction with ZnO and ZrO_2 promotes the metal dispersion and stabilization of $Cu^{\delta+}$ sites at the metal/oxides interface, which also influences the redox properties and reactivity of Cu/ZnO/ZrO_2 catalyst system. The presence of Cu^0, $Cu^{\delta+}$ and Lewis acid sites on the Cu/ZnO/ZrO_2 catalyst also led to the activation of H_2, CO_2 and CO during the reaction [30].

The effect of reduction temperature of Pd–CeO_2 on the activity and selectivity for CO_2 hydrogenation has been studied by Shen et al.[31]. They found that the reduction temperature influenced both the structural properties and the catalytic behavior of Pd–CeO_2 catalyst. At the reduction temperature of 500 °C, the overall conversion of CO_2 was reduced and the product selectivity has significantly changed. This was because during high temperature, the palladium surface was greatly changed due to the reduction of ceria species between CeO_2 and Ce_2O_3 as well as the increase of palladium particles. The decrease in CO_2 conversion was significant due to the weak interaction between the Pd and ceria support which was caused by the significant Pd particles growth, together with sintering of ceria as support. At high temperature treatment, the Ce^{3+} species act as active sites for dissociation of CO_2 to form carbon monoxide and subsequently decreased production of methanol [31]. Synthesis of ZnO/Al_2O_3 from mixtures of ZnO and $ZnAl_2O_4$ has been done by Park et al. [32]. They reported that the presence of large particle size of ZnO in ZnO/Al_2O_3 synthesis from high composition ratio of Zn and Al could give high activity in CO_2 hydrogenation. However, the parent $ZnAl_2O_4$ showed a highly stable performance with no deactivation for 240 h compared to ZnO/Al_2O_3. The deactivation was strongly related to the agglomeration of ZnO during the reduction treatment at 850 °C, which hindered the ZnO reduction [32].

2.4. Addition of chemical precursors

The use of precursors in catalyst preparation can control the conditions of co-precipitation and influence the catalytic behavior [12]. The activity of Cu/ZnO catalyst for methanol formation depended on the precursor structure. Toyir et al. [12] reported that the presence of precursors like methoxide or acetylacetonate salts in the preparation of SiO_2 or ZrO supported catalyst during impregnation could enhance the catalytic performance in CO_2 hydrogenation to methanol. The presence of metallic precursors could determine the final characteristic and give a higher dispersion of metal in catalyst. In the stage prior to the impregnation, the interaction between the precursor and support could be improved and after the calcination step, the catalysts have only the supported mixed oxides without any precursor anions.

Cu/ZnO catalysts were prepared by the co-precipitates of zincian–malachite and aurichalcite as hydroxycarbonate precursors as reported by Fujita et al. [14]. At low heating rates, a very small crystallite of CuO was generated in the presence of aurichalcite and no effect was found on the catalyst synthesized from zinc–malachite. Positive effects of aurichalcite precursor have also been found by Fujitani and Nakamura [17], which exhibited an excellent catalytic activity with 7.56% of methanol yield due to the automatic mixing between the Cu and Zn in the compound.

Guo et al. [19] prepared CuO–ZnO–ZrO_2 catalyst via urea–nitrate combustion method, and the prepared catalyst has favorable characteristics such as small grain size, high surface area and low reduction temperature. The presence of urea in the combustion process might distribute some heat, which renders the rapid quenching effect forming smaller CuO particles and more favorable interaction between copper species and ZnO, ZrO_2. The increase of urea content leads to the increase of partial transformation of *t*-ZrO_2 to *m*-ZrO_2 supported catalyst resulting in improved methanol selectivity from CO_2 hydrogenation [18,19]. Raudaskoski et al. [4] observed that the activity of Cu catalysts support on *m*-ZrO_2 for methanol synthesis from CO_2 and H_2 was 4.5 times greater than that of *t*-ZrO_2. The higher rate of methanol synthesis over the Cu/*m*-ZrO_2 could be solely due to the higher active intermediates concentration that occurred on the catalysts [4,33].

Recently, Guo et al. [18] have synthesized CuO–ZnO–ZrO_2 catalysts by glycine–nitrate combustion, which is reported as a simple, fast and effective preparation method. The amount of glycine added greatly influenced the combustion process and the catalyst properties due to the role of glycine as a fuel in the combustion reaction and has significant effects on the formation of zirconia phase. The catalyst content of 50% glycine-nitrate exhibited an optimum activity of 16% and 10% of CO_2 conversion and methanol yield, respectively. In their experiments, CuO–ZnO–ZrO_2 catalyst synthesized by glycine–nitrate combustion [18] was more effective than urea–nitrate combustion method [19] for CO_2 hydrogenation to methanol. This was due to the presence of metal nitrate and glycine in the combustion process that act as an oxidant and fuel, respectively compared to the urea alone, which only acts as a fuel. A thermally redox reaction in the combustion synthesis process occurred between an oxidant and fuel and their characteristics were strongly depended on the fuel selection [18,34,35].

2.5. Water as an exhibitor

The poor performance of CO_2 hydrogenation catalyst is mostly due to the presence of water during the CO_2 hydrogenation reaction. During the methanol formation via CO_2 hydrogenation, CO was serving as the CO_2 source and scavenger of oxygen atoms from water molecules, which then act as inhibitor of the active metal sites [29,30]. Sloczynksi et al. [27] found that the addition or total replacement of Al_2O_3 by ZrO_2 to Cu/ZnO/Al_2O_3 could increase the methanol yield due to the direct decrease of H_2O adsorption on the catalysts. It was strongly due to the poor specific functionality and hydrophilic character of alumina, which showed marked positive effect of water towards active site stability. The formation of dimethyl ether (DME), which was produced from methanol dehydration at high temperature, seemed to be limited during the RWGS [12]. The presence of water during methanol synthesis accelerated the crystallization growth of metal oxide and led to the deactivation of the catalyst and non-adsorption of CO_2 [14,25]. Nonetheless,

Table 1
Various heterogeneous catalysts for methanol synthesis from CO_2 hydrogenation.

Catalyst	Method preparation	Reaction condition			Reaction results		Ref.
		Pressure (MPa)	Temperature (°C)	Time (h)	CO_2 conversion (%)	Methanol yield (%)	
Cu–Zn/SiO_2	Impregnation	2	270	Na	2.0	0.94	[12]
Cu–Zn–Ga/SiO_2	Impregnation	2	270	Na	2.0	2.0	[12]
Cu–Ga/ZnO	Impregnation	2	270	Na	2.0	1.11	[12]
Cu/ZnO	Co-impregnation of methoxide	2	270	20	2.2	2.2	[13]
Cu–Ga/ZnO	Co-impregnation of methoxide	2	270	20	6.0	5.28	[13]
Cu–Zn–Ga/SiO_2	Co-impregnation of methoxide	2	270	20	3.4	2.58	[13]
Cu–V/γ-Al_2O_3	Impregnation	3	240	Na	12	3.0	[15]
Cu/ZnO	Physical mixture	5	250	Na	Na	7.56	[17]
CuO–ZnO–ZrO2	Glycine-nitrate combustion	3	240	Na	16	10.0	[18]
CuO–ZnO–ZrO_2	Urea-nitrate combustion	3	240	Na	17	9.6	[19]
Cu/SiO2	Physical mixture	1.25	250	Na	Na	0.5	[21]
(Zn)Cu/SiO_2	Physical mixture	1.25	250	Na	Na	1.8	[21]
Cu/ZnO/ZrO_2	Co-precipitation	8	220	Na	21	14.3	[26]
Ag/ZnO/ZrO_2	Co-precipitation	8	220	Na	2	1.9	[26]
Au/ZnO/ZrO_2	Co-precipitation	8	220	Na	2.5	1.5	[26]
Cu/ZnO/$ZrO_2Ga_2O_3$	Co-precipitation	8	220	Na	Na	42.0	[27]
Cu/ZnO/ZrO_2MnO	Co-precipitation	8	220	Na	Na	30.0	[27]
Cu/ZnO/$ZrO_2B_2O_3$	Co-precipitation	8	220	Na	Na	35.0	[27]
Cu/ZnO/$ZrO_2In_2O_3$	Co-precipitation	8	220	Na	Na	9.0	[27]
Cu/ZnO/$ZrO_2Gd_2O_3$	Co-precipitation	8	220	Na	Na	31.0	[27]
Cu/ZnO/$ZrO_2Y_2O_3$	Co-precipitation	8	220	Na	Na	38.0	[27]
Cu/ZnO/$ZrO_2Ga_2O_3$	Complexing with citric acid	8	220	Na	Na	41.0	[27]
Cu/ZnO/ZrO_2MnO	Complexing with citric acid	8	220	Na	Na	31.0	[27]
$YBa_2Cu_3O_7$	Grinding stoichiometric	3	240	Na	3.4	1.72	[28]
Cu/ZnO/ZrO_2	Reverse co-precipitation under ultrasound irradiation	3	240	Na	17.5	8.5	[29]
Cu/ZnO/Al_2O_3	Commercial	3	240	Na	15.9	7.7	[29]
Cu/ZnO/ZrO_2	Reverse co-precipitation under ultrasound irradiation	1	200	Na	3.2	2.1	[30]
Pd–CeO_2	Impregnation	2	250	Na	4.1	1.2	[31]

high concentration of CO during the reaction produced only small amount of water that prohibited the crystallization of catalyst [25]. Based on thermodynamics, the increase of CO_2 concentration in the feed gas could lead to an increase in the yield of water and a decrease in the yield of methanol [4,25].

Table 1 summarizes various heterogeneous catalysts used for synthesis of methanol from CO_2. The data showed that Cu and ZnO are the most popular metals used in the hydrogenation of methanol catalysts. This could be attributed to the Cu–Zn active sites on the metal surface which were necessary in the formation of methanol as proposed by Kakumoto and Watanabe [20]. Cu/ZnO/$ZrO_2Ga_2O_3$ prepared by co-precipitation method possessed the best catalytic performance with 42.0% yield of methanol. In conclusion, the low activity of catalysts was due to the lack or altering of active centers number and the catalysts energetic characteristics to overcome the CO_2 activation problems in hydrogenation process.

3. Synthesis of cyclic carbonate (ethylene carbonate, propylene carbonate and styrene carbonate)

The synthesis of cyclic carbonates by CO_2 cycloaddition to epoxides (Fig. 2) has received much attention in terms of "green chemistry" and "atom economy" as there is no formation of by-product and this is also one of the CO_2 chemical fixation methods [11,36]. Cyclic carbonates such as ethylene carbonate (EC) propylene carbonate (PC) and styrene carbonate (SC) have been used as polar solvents, precursors for polycarbonate materials synthesis, electrolytes in lithium secondary batteries, in the production of pharmaceutical, and as raw materials in various chemical reactions [11,37,38]. The synthesis of cyclic carbonates has been successfully performed via coupling reaction of CO_2 and epoxides in the industry [11,37]. The reactions of CO_2 with glycol and CO_2 oxidative carboxylation of olefin are two possible routes for synthesis of cyclic carbonates [11,39].

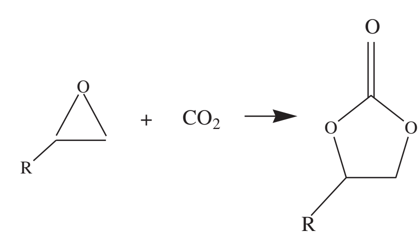


Fig. 2. Cycloaddition of CO_2 to epoxides [11,36].

Both homogeneous and heterogeneous catalysts systems have been developed for cyclic carbonate production from CO_2 including amines [40], quaternary ammonium salts [41–43], polyfluoroalkyl phosphonium iodides [44], ionic liquids [45,46], porphyrin [47–49], phthalocyanine [50], phosphines [51] and organometallic complexes [52]. However, these catalysts normally suffer from problems such as low catalyst stability and activity, air sensitivity, need to co-solvent or co-catalyst and also requirement of high pressure and/or temperature for the reaction [38,53]. The development of highly efficient and environmentally benign catalysts with easy separation and recycling for the reaction of epoxides with CO_2 still remains as a challenge.

3.1. *Advantages of ionic liquids*

The applications of ionic liquids in both the chemical industries and the academia received more attention due to their

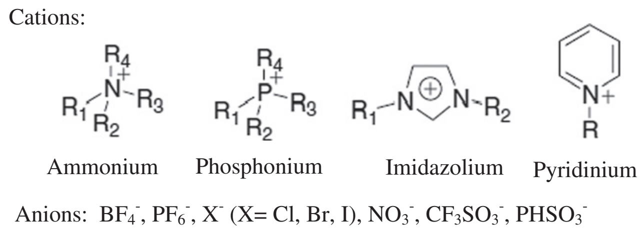


Fig. 3. Some of the ionic liquids used in synthesis of cyclic carbonate [54,58,59].

magical advantages including excellent thermal stability, negligible vapor pressure, diversity, recyclability and immiscibility with some of the organic and inorganic materials [38,54–56]. Ionic liquids are able to dissolve a variety of materials such as proteins, surfactants, salts, sugars, amino acids and polysaccharides and act as solvents to dissolve organic molecules likes plastics, DNA and crude oil [56,57]. The CO_2 can dissolve into the ionic liquid phase, making the reactions between CO_2 and ionic liquids possible and appropriate [54]. Various ionic liquids such as quaternary ammonium, phosphonium, imidazolium, pyridinium and their possible anions have been reported in the literature for the synthesis of cyclic carbonates from cycloaddition of CO_2 to epoxides (Fig. 3) [54,58,59]. The immobilization of ionic liquids into solid supports as an alternative method in the development of efficient catalysts for cycloaddition of CO_2 to epoxides has been reported [11,37,38,60].

3.2. *Catalytic performance*

3.2.1. *Supported ionic liquid catalysts*

Xie et al. [38] developed a novel catalyst system of hexabutylguanidinium bromide/$ZnBr_2$ under mild conditions with air stability, cheap and environmentally benign system as well as with no additional co-solvents. The catalyst exhibited high activity for the synthesis of cyclic carbonates from cycloaddition of CO_2 and epoxides, and it could be reused up to five times without significant change in the yield or selectivity [38]. The high catalytic performance of the catalyst has resulted from special steric and electrophilic characteristics of hexabutylguanidinium bromide ionic liquid. This novel catalyst system was efficient for the synthesis of styrene carbonate via cycloaddition of unreactive styrene oxide with CO_2. Compared to the propylene oxide, styrene oxide is a bulky epoxide and its β-carbon atom has low reactivity which makes lower transformation to styrene carbonate [38].

The use of grafted SiO_2 as a support for ionic liquid of 3-*n*-butyl-1-propyl-imidazolium with various metal salts acting as co-catalyst was reported by Xiao et al. [37]. The presence of cations and anions of co-catalyst did not influence the propylene carbonate selectivity, but enhanced the propylene carbonate yield to more than 98%. With the Cl^- as a common anion, the activity of cations towards propylene carbonate decreased in the order of $Zn^{2+} > Ni^{2+} > Co^{2+} > Fe^{3+} \approx Cu^{2+} \approx Al^{3+} > Cu^+$. While Zn^{2+} acts as a common anion, the propylene carbonate decreased in the order of $Br^- \approx Cl^- > OAc^- > SO_4^{2-}$ [37]. Most of the catalysts can be reused two times and the propylene carbonate yield was significantly decreased at about 10%. The less reusability and performance of those catalysts could be attributed to the loss of ionic liquid in the catalyst systems.

Wang et al. [42,61] reported that the ionic liquid of quaternary ammonium and imidazolium salts supported on SiO_2 were highly efficient for propylene carbonate production from CO_2 and epoxides. This was due to the synergistic effect that occurred between the support and quaternary ammonium salts which led to the activation of CO_2 molecules and propylene oxide [42]. Meanwhile, the activity of quaternary ammonium salts without support was strongly depended on the type of anions in order of n-$Bu_4NBr >$ n-$Bu_4NI \approx n$-$Bu_4NCl > n$-Bu_4NF [42]. It has been concluded that the activity of the anions was in good agreement with the order of nucleophilicity of anion except for n-Bu_4NI. However, little effect was observed among the silica-supported ionic liquid catalysts counterparts. These researchers also studied the effect of various alkyl groups (Me_4NBr, Et_4NBr, n-Pr_4NBr, and n-Bu_4NBr) in quaternary ammonium bromides and observed that the length of alkyl group had little influence on the cycloaddition reaction. All the cations supported on SiO_2 were highly active for the synthesis of propylene carbonate except for Me_4NBr [42]. This was possibly due to the existing major side reaction of propylene oxide isomerization, which led to a reduction of propylene carbonate yield [42].

One-pot synthesis of cyclic carbonates via coupling reaction of CO_2 and styrene oxide with the presence of Au/SiO_2, zinc bromide, and tetrabutylammonium bromide (Bu_4NBr) in catalyst system without any organic solvent has also been reported [62]. This method becomes more interesting and economical due to the preliminary synthesis and the epoxides isolation could be avoided [62]. In the catalyst system, Au/SiO_2 acts as an active site for the epoxidation of styrene, while zinc bromide and Bu_4NBr considerably catalyze the subsequent cycloaddition of CO_2 to epoxide. The presence of catalyst system greatly enhanced the transformation of styrene oxide to styrene carbonate in a short reaction time and a low reaction temperature of 30 min and 80 °C, respectively [62]. Moreover, there was no increase of product yield when the amount of Au/SiO_2 was increased up to 0.1 g, although the amounts of $ZnBr_2$ and Bu_4NBr were doubled. They also studied the highly efficient catalyst system consisting of $ZnBr_2$/n-Bu_4NI with an optimum ratio of the two at similar reaction and condition, in which 100% selectivity and almost 100% yield of styrene carbonate have been achieved [63].

Kawanami et al. [46] reported that BF_4^- was the most highly active catalyst among the anions (NO_3^-, $CF_3SO_3^-$, BF_4^- and PF_6^-) of imidazolium salts for cyclic carbonate synthesis. Similar results have been obtained using different anions of 1-alkyl-3-methylimidazolium salts [C_4-mim] supported on SiO_2 ($BF_4^- > Br^- > PF_6^-$) [61]. It has been observed that low reactivity of β-carbon atom in the propylene carbonate could be activated more in the presence of ionic liquid of BF_4^- anion [46]. The ionic liquid quantity could affect the reaction coupling of carbon dioxide and epoxides for cyclic carbonate synthesis [37]. The increase in the amount of immobilized ionic liquid on metallic salts could increase the propylene oxide conversion [64]. However, only a small increase in the conversion was achieved in the presence of more than 1 g of supported ionic liquid, due to the excessive immobilized ionic liquid on the surface of catalyst [37].

The effect of catalyst acidity for the coupling reaction of CO_2 with epoxides has also been reported [38,65]. Lu et al. [65] found that the presence of Lewis base or quaternary salt of catalyst could enhance the catalytic activity for synthesis of ethylene carbonates from supercritical CO_2 and ethylene oxide (EO) mixture. The catalysts were prepared by tetradentate schiff-base metal complexes which were denoted as metal-Salen. The binary catalyst consisting of salenAl-$(OCH_2CH_2)_3Cl$ and n-Bu_4NBr was found to be the most effective catalyst in comparison to the other substituted aluminum-Salen complexes in the order of SalenAlCl > Salen(Cl)AlCl > Salen(NO_2)AlCl > Salen(*t*-Bu)AlCl. It was concluded that the substitution on the SalenAlX aromatic rings could have a negative effect on the activity. However, the existence of halides or long oxyethylene chain in axial X-group led to the improved catalytic activity of parent SalenAlX [65]. The catalytic activities of metal-Salen complexes in the presence of quaternary salt as co-catalyst were in the following order: SalenCrCl > SalenCo > SalenNi > SalenMg, SalenCu, SalenZn [65]. This finding could be attributed to the high coordinative activity between the salen ligands and metallic ions, where the salen

ligands have two coordinate covalent sites located in a planar array [65]. Bifunctional nucleophile–electrophile SalenAlX coupled with quaternary ammonium salt (n-Bu_4NY) without any organic solvent under mild temperature and pressure was found to be effective for the reaction [53]. This was due to the moderate electrophilicity and nucleophilicity together with high leaving ability of nucleophile in the catalyst system [53].

The development of heterogeneous catalyst using natural biopolymers as supports has also got much attention. The performance of chitosan-supported quaternary ammonium catalyst was shown to be dependent on the anions of salts, whose activity decreased in the order of $I^- > Br^- > Cl^-$ [60]. This was related to the leaving ability and nucleophilicity of anions in ionic salts. The chitosan as support played an important role in the synthesis of propylene carbonate; however, it did not demonstrate any catalytic activity when present alone. Various ionic liquids loaded on suitable supports in synthesis of cyclic carbonate from CO_2 are summarized in Table 2. Most of the supports that were used are SiO_2, due to the very low permeability to gases and ionic contaminants. Ionic liquid of 2-hydroxypropyl triethylammonium iodide supported on chitosan gave the best performance with 100% yield of propylene carbonate and the catalyst could be recycled up to 5 times. Generally, the catalytic performances over the supported ionic liquid catalysts are much higher due to the surface bond between the support and ionic liquid which affects the active sites of the catalyst. Moreover, the ionic salts also cause the ring-opening of epoxides and the metallic cation catalyze the formation of cyclic carbonate.

3.2.2. Supported mesoporous catalysts

The use of mesoporous materials as supports, such as MCM-41 for cyclic carbonates synthesis from CO_2 and epoxides has been reported as well [40,66,67]. The combination of aluminum phthalocyanine complex with n-Bu_4NBr quaternary ammonium salt as co-catalyst on MCM-41 could enhance the catalytic activity and stability of the catalyst. The catalyst could be reused for ten recycles without any significant change in the activity. The combination of both materials could also lead to the epoxides ring-opening and CO_2 activation to form corresponding cyclic carbonates. The catalytic reaction mechanism was already discussed by Lu et al. [66]. They also reported the effect of the catalysts in production of cyclic carbonates from CO_2 and various epoxides, and gave the high catalytic activity in the order of $CH_2Cl > H > Ph > CH_3$ [66]. The immobilization of cobalt complex with a quaternary ammonium salt supported on MCM-41 exhibited good stability and activity (100% ethylene carbonate selectivity). The catalyst has been operated for a whole day with similar activity [67]. This was due to the synergistic effect occurred in catalytic system during ethylene carbonate formation [67].

Another investigation conducted by Yasuda et al. [68], showed that the impregnation of samarium on ZrO_2 gave the highest catalytic performance which was due to the high dispersion of samarium oxychloride (SmOC1) on the surface of ZrO_2 [68]. A highly active and reusable catalyst of Ti-SBA-15 modified with adenine to avoid the use of solvents and co-catalysts such as *N*,*N*-dimethylaminopyridine (DMAP) and quaternary ammonium salts was studied by Srivastava et al. [69]. The CO_2 molecules were activated by the nitrogen groups of adenine, which then reacted with epoxides adsorbed on the surface of silica SBA-15 to form cyclic carbonates. Meanwhile, Ti_4^+ enhanced the potential adsorption of epoxides substrate on CO_2 molecules and subsequently increased the catalytic activity of catalyst [69].

3.3. Other heterogeneous catalysts

The use of zinc chloride supported on chitosan with 1-butyl-3-methylimidazole halides (BMImX) as co-catalyst without any organic solvents to form cyclic carbonates has been reported by

Table 2
Various ionic liquids loaded on suitable supports in synthesis of cyclic carbonate from CO_2 and epoxides.

Ionic liquids	Support	Reaction condition				Reaction results			Ref.
		Solvent or co-catalyst	Pressure (Mpa)	Temperature (°C)	Time (h)	Cyclic carbonate yield (%)	TOF (h^{-1})	Recycle	
3-*n*-butyl-1-propyl-imidazolium bromide	SiO_2	$ZnCl_2$	1.5	110	1	95[a]	2712	2	[37]
3-*n*-butyl-1-propyl-imidazolium bromide	SiO_2	$ZnBr_2$	1.5	110	1	96[a]	2741	2	[37]
3-*n*-butyl-1-propyl-imidazolium bromide	SiO_2	$Zn(OAc)_2$	1.5	110	1	84[a]	2398	2	[37]
3-*n*-butyl-1-propyl-imidazolium bromide	SiO_2	$ZnSO_4$	1.5	110	1	85[a]	2741	2	[37]
3-*n*-butyl-1-propyl-imidazolium bromide	SiO_2	$NiCl_2$	1.5	110	1	71[a]	2027	2	[37]
3-*n*-butyl-1-propyl-imidazolium bromide	SiO_2	$CuCl_2$	1.5	110	1	55[a]	1570	2	[37]
3-*n*-butyl-1-propyl-imidazolium bromide	SiO_2	$AlCl_3$	1.5	110	1	54[a]	1542	2	[37]
3-*n*-butyl-1-propyl-imidazolium bromide	SiO_2	CuCl	1.5	110	1	50[a]	1428	2	[37]
3-*n*-butyl-1-propyl-imidazolium bromide	SiO_2	$CoCl_2$	1.5	110	1	67[a]	1913	2	[37]
3-*n*-butyl-1-propyl-imidazolium bromide	SiO_2	$FeCl_3$	1.5	110	1	55[a]	1570	2	[37]
Hexabutylguanidinium bromide	$ZnBr_2$	Na	3	130	1	95[b]	6627	5	[38]
Hexabutylguanidinium bromide	$ZnBr_2$	Na	3	130	1	80[a]	8566	5	[38]
Tetra-n-butyl ammonium bromine	SiO_2	Na	8	150	10	97[a]	Na	4	[42]
Tetra-n-butyl ammonium Chloride	SiO_2	Na	8	150	10	90[a]	Na	4	[42]
Tetra-n-butyl ammonium Iodide	SiO_2	Na	8	150	10	96[a]	Na	4	[42]
Tetra-n-butyl ammonium Fluoride	SiO_2	Na	8	150	10	84[a]	Na	4	[42]
Me_4NBr	SiO_2	Na	8	150	10	96[a]	Na	4	[42]
Et_4NBr	SiO_2	Na	8	150	10	96[a]	Na	4	[42]
n-Pr_4NBr	SiO_2	Na	8	150	10	97[a]	Na	4	[42]
n-Bu_4NBr	SiO_2	Na	8	150	10	97[a]	Na	4	[42]
2-hydroxypropyl triethylammonium chloride	Chitosan	Na	4	140	6	73[a]	Na	5	[60]
2-hydroxypropyl triethylammonium bromide	Chitosan	Na	4	140	6	95[a]	Na	5	[60]
2-hydroxypropyl triethylammonium iodide	Chitosan	Na	4	140	6	100[a]	Na	5	[60]
$[C_4\text{-mim}]^+[BF4]^-$	SiO_2	Na	8	160	4	96	Na	4	[61]
$[C_4\text{-mim}]^+[PF6]^-$	SiO_2	Na	8	160	4	93	Na	4	[61]
$[C_4\text{-mim}]^+Br^-$	SiO_2	Na	8	160	4	95	Na	4	[61]
$C_3H_6\text{-}P(n\text{-}Bu)_3Br$	SiO_2	Na	10	160	5	99[a]	Na	Na	[71]

[a] Propylene carbonate.
[b] Styrene carbonate.

Xiao et al. [70]. The catalyst system could be recycled up to five times with the selectivity of propylene carbonate was remaining at >99%, but the catalytic activity was slightly lower. However, the BMImBr has to be added for every recycle process to retain the constant performance of chitosan-supported zinc chloride catalyst during the reaction [70]. Similar synergistic effect of SiO_2-immobolized phosphonium halides on synthesis of propylene carbonate from CO_2 and propylene oxide (PO) has also been reported by Takahashi et al. [71].

Organometallic complexes such as Cr, Co, Ni, Al, Mn, Zn, Ru, and Re loaded on various suitable supports as heterogeneous catalysts have been reported for the synthesis of cyclic carbonates from CO_2. Recently, Bai et al. [72] developed bifunctional metalloporphyrins catalyst by loading various metals (Co, Fe, Mn, and Cr) and the catalysts could be reused for five times. Among them, cobalt porphyrin was found to be the optimal catalyst with a poly carbonates yield of 95.4% within 5 h. The activity of bifunctional metalloporphyrin catalyst towards poly carbonates yield in the order of Co > Mn > Fe > Cr due to the acid center of the metal that catalyzed the reaction step to form the cyclic carbonate. The catalyst system consisting of $ZnCl_2$ and phosphonium halides for coupling reaction of epoxides and CO_2 has been studied by Sun et al. [73]. $ZnCl_2/PPh_3C_6H_{13}Br$ catalyst gave high conversion with more than 99.0% selectivity, excellent stability and high turnover frequency (TOF). Xie et al. [38] reported that the combination of Zn and Br gave the most suitable Lewis acid catalyst to increase the catalytic activity compared to $FeBr_3$, $ZnCl_2$, and ZnI_2. Zhang et al. [74] observed that the activation of epoxides occurred via binding to Lewis acid metal center had a synergistic effect between them. This phenomenon resulted in epoxides ring-opening when the nucleophiles attack the alcoholate CO_2 at the carbon atom [74]. Various heterogeneous catalysts for cyclic carbonates synthesis from CO_2 and epoxides are tabulated in Table 3. As can be seen, the mesoporous nanoparticles in the catalyst system were used up to 10 times due to their high thermal and hydrothermal stability.

3.4. Effects of reaction temperature and CO_2 pressure

The catalytic activity of the catalyst system in chemical fixation of CO_2 and epoxides to cyclic carbonate is very sensitive to the reaction temperatures and the formation rate of cyclic carbonate increases with the enhancement of reaction temperature [37,38,62,65]. Hexabutylguanidinium bromide/$ZnBr_2$ catalyst showed better activity with high turnover frequencies (TOF) with increasing reaction temperatures, and the optimum temperature was found at 130 °C [38]. Similar phenomenon was found by Xiao et al. [37] for the synthesis of propylene carbonate from chemical fixation of carbon dioxide with propylene oxide. However, the activity of catalyst only slightly increased the reaction at temperature up to 110 °C [37]. For styrene carbonate, Sun et al. [62] found that the reaction temperature was at 80 °C and the increase of temperature up to 90 °C led to the decrease in the styrene carbonate yield. This was related to the by-products formation and complete decomposition of the oxidant during the high temperature which caused the low yield of cyclic carbonate [62]. The olefin epoxidation was proven to be parallel with the benzaldehyde formation by the cleavage of the C–C bond. In addition, the cycloaddition of CO_2 to form styrene oxide was faster than the epoxidation process, thus, the formation of styrene carbonate and benzaldehyde was increased similarly with time [62].

The carbon dioxide pressure also has a significant role in cyclic carbonates synthesis via the coupling reaction of CO_2 and epoxides [38]. The highest catalytic activity for the reaction could be attained typically at an operating pressure between 1.5 and 3.0 MPa, depending on the operating and catalytic systems [37,38]. Increasing or decreasing the CO_2 pressure from the optimum value will lower the catalytic activity, the reason being the excessive CO_2 pressure which may slow down the epoxides interaction with the catalyst, thus attributing to low catalytic activity [37,38]. For instance, the conversion and yield of styrene carbonate increase to 89% and 35% at 1 MPa of CO_2 pressure and atmospheric pressure, respectively. The conversion and yields were not significantly affected when the CO_2 pressure was in the range between 1 and 12 MPa. However, at 15 MPa, both the conversion and styrene carbonate yield decreased due to the phase change in the reaction mixture, which led to an increase in the volume during the reaction process. This would make the concentration of substrate low and reduce the styrene oxide conversion and styrene carbonate yield. Moreover, high pressure of CO_2 tended to produce much oligomer that was able to change the reaction volume and properties of the liquid and CO_2 gas phases [38,64].

Table 3
Various heterogeneous catalysts for synthesis of cyclic carbonates from CO_2 and epoxides.

Catalyst	Reaction condition				Reaction results				Ref.
	Solvent or co-catalyst	Pressure (MPa)	Temperature (°C)	Time (h)	Cyclic carbonate selectivity (%)	Cyclic carbonate yield (%)	TOF (h^{-1})	Recycle	
Guanidine-MCM-41	CH_3CN	5	140	70	92	90.0[a]	Na	3	[40]
ClAlPc-MCM-41	n-Bu_4NBr	4	110	2	Na	Na[b]	415	10	[66]
ClAlPc-MCM-41	n-Bu_4NBr	4	110	2	Na	Na[c]	384	Na	[67]
SalenCo(II)-MCM-41	n-Bu_4NBr	12.5	110	Na	100	85.6[b]	Na	Na	[67]
Sm(O,C1)/ZrO_2	Na	14	200	8	97.6	23.9[c]	Na	Na	[68]
Sm(O,Cl)/SiO_2	Na	14	200	8	60.7	3.3[c]	Na	Na	[68]
Ti-SBA-15-adenine	CH_3CN	0.69	120	6	100[c]	Na	Na	10	[69]
Ti-SBA-15-adenine	CH_3CN	0.69	120	8	87[a]	Na	Na	10	[69]
$ZnCl_2$/chitosan	BMImBr	1.5	110	1	99	95[c]	2712	5	[70]
Co/porphyrin	MeOH	0.7	80	5	99	95.4[c]	190.8	5	[72]
Fe/porphyrin	MeOH	0.7	80	15	99	73.5[c]	49.0	5	[72]
Mn/Porphyrin	MeOH	0.7	80	5	99	86.5[c]	173.0	5	[72]
Cr/porphyrin	MeOH	0.7	80	24	99	12.3[c]	5.1	5	[72]
$ZnCl_2/PPh_3C_6H_{13}Br$	Na	1.5	120	1	99	96.0[c]	4718.4	5	[73]
$ZnCl_2/PPh_3C_5H_{11}Cl$	Na	1.5	120	1	99	70.0	3440.5	5	[73]
$ZnCl_2/PPh_3C_4H_9I$	Na	1.5	120	1	99	95.1	4674.1	5	[73]

[a] Styrene carbonate.
[b] Ethylene carbonate.
[c] Propylene carbonate.

4. Synthesis of dimethyl carbonate (DMC)

Dimethyl carbonate (DMC) is non-toxic, biodegradable and environmentally benign compound and DMC is widely used in industry for production of polycarbonate, polyurethane and other chemicals [5,75,76]. It is also an ideal additive to gasoline or fuel oil for transportation due to its high oxygen content (53%) and octane number [76–78]. Commercially, there are three processes for the production of DMC: (i) direct synthesis of DMC from CO_2 and methanol; (ii) synthesis of DMC from CO_2, methanol and epoxides; (iii) synthesis of DMC from CO_2 and acetals or ortho-ester [11]. DMC produced via the reaction of methanol and toxic phosgene is subsequently improved by non-phosgene route of carboxylation of methanol [76]. However, the process is hazardous because of the use of a highly flammable reactant mixture and toxic chemicals.

4.1. Direct synthesis of DMC from CO_2 and methanol

The direct synthesis of DMC from methanol and CO_2 has attracted considerable attention as one of the options to overcome the global warming and also for the development of carbon resources [5,76]. It is difficult to obtain high performance of catalyst in the production of DMC due to the high thermodynamic stability of CO_2 and catalyst deactivation [5,76,77].

$$2CH_3OH + CO_2 = (CH_3O)_2CO + H_2O \quad (3)$$

Various types of heterogeneous catalysts have been developed for the production of DMC via CO_2 and methanol. ZrO_2 catalysts have unique properties and are effective for production of DMC from methanol and CO_2 [5]. Tomishige et al. [79] reported that the neighboring acidic and basic sites on ZrO_2, observed by TPD results of CO_2 and NH_3 co-adsorption, act as active sites in the formation of DMC. The formation mechanism of DMC from methanol and CO_2 over ZrO_2 catalyst using in situ infrared spectroscopy has been investigated by Jung and Bell [80] and is shown in Fig. 4. The presence of Brönsted basic hydroxyl group (Zr–OH) and coordinately unsaturated $Zr^{4+}O^{2-}$ on the ZrO_2 were effective for the production of DMC from CO_2 and methanol feedstock [80].

The modified ZrO_2 based catalyst has been explored in order to enhance the catalytic activity in the reaction. The addition of phosphoric acid (H_3PO_4) to ZrO_2 for DMC synthesis was reported by Ikeda et al. [81] showing that the acid–base bifunctional properties of H_3PO_4/ZrO_2 and catalyst calcination temperature were the two parameters that influenced the catalytic activity. Tomishige et al. [82] found a similar observation on the effect of calcination temperature on the CeO_2–ZrO_2 catalyst, in which the increase of calcination temperature would form larger catalyst crystal size and higher catalytic activity for DMC formation. The calcination temperature however did not influence the tetragonal and the bulk structure of the binary CeO_2–ZrO_2 catalyst.

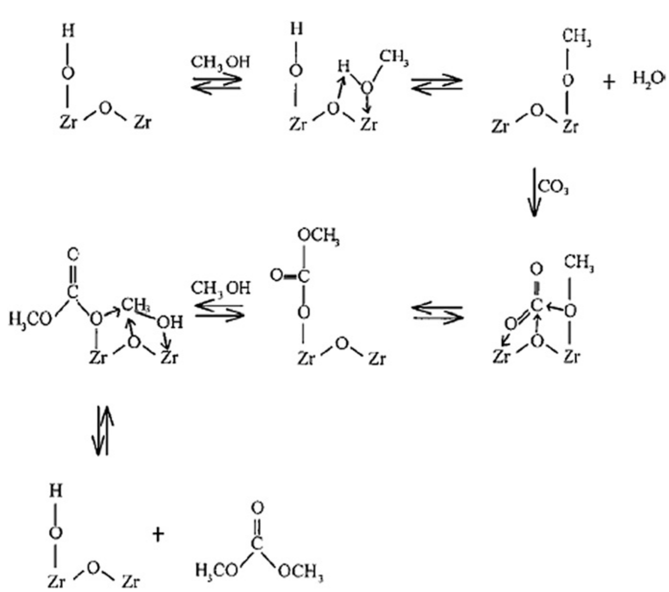


Fig. 4. Mechanism for the formation of DMC from CH_3OH and CO_2 over ZrO_2 [80].

Bian et al. [83] concluded that the activation of CH_3OH and CO_2 was most favorable with the increase of the reaction temperature. Nevertheless, the DMC yield decreased dramatically when the reaction temperature increased more than the optimum value due to the reduction of CO_2 adsorption on the catalyst surface. Further investigation on CeO_2–ZrO_2 catalyst with the addition of 2,2-dimethoxy propane (DMP) to the reaction system of DMC synthesis has been done by Tomishige et al. [84]. The appropriate amount of DMP was effective for water removal in the reaction system and enhanced the DMC yield due to the equilibrium level which occurred during the reaction between DMP and water [84]. Jiang et al. [85] reported the effective synthesis of DMC over Keggin unit, 12-tungstophosphoric acid/zirconia ($H_3PW_{12}O_{40}/ZrO_2$). The activity of catalysts which were prepared under mild condition sol–gel method increased linearly with an increase of $H_3PW_{12}O_{40}$ content on catalyst up to 50 mg. The characteristic of weak Brönsted acid sites in the $H_3PW_{12}O_{40}/ZrO_2$ indicated that this catalyst was ninefold more effective than ZrO_2 in methanol activation [85].

The performance of metal oxide catalysts in the production of DMC from CO_2 and methanol has been reported by La and Song [86]. The catalytic effectiveness of metal oxides in the order of $Ce_{0.1}Ti_{0.9}O_2 > Ce_xTi_{1-x}O_2$ $(x=0.2–0.8) > ZrO_2 > CeO_2 > TiO_2$ has been observed. The stabilization of crystalline phase of $Ce_{0.1}Ti_{0.9}O_2$ could enhance the activity performance of the catalyst. The addition of $H_3PW_{12}O_{40}$ on $Ce_{0.1}Ti_{0.9}O_2$ showed the highest catalytic performance when compared to that of $H_3PW_{12}O_{40}$/ZrO2 and $Ce_{0.1}Ti_{0.9}O_2$ due to the Brönsted acid and base sites of $H_3PW_{12}O_{40}/Ce_{0.1}Ti_{0.9}O_2$ catalyst measured by NH_3 and CO_2-TPD provided by $H_3PW_{12}O_{40}$ and $Ce_xTi_{1-x}O_2$, respectively [86,87]. The supported bimetallic catalysts could allow for systematic altering of the size, electronic structure, absorption characteristics, reducibility and deactivation behavior of a catalyst [88,89]. Other heterogeneous catalysts such as Ni–Cu/MoSiO and Ni–Cu/VSiO catalysts were also effective in DMC synthesis directly from CO_2 and methanol [90]. The proper surface sites of catalyst is important for good reaction rates of about 15% of CH_3OH conversion and over 85% of DMC selectivity. Furthermore, the metallic site M (Ni–Cu alloy), Lewis acid site M^{n+} (Mo^{6+} or V^{5+}) and Lewis base site M–O (Mo–O or V–O) on the catalysts surface and the changes in their d-electron density play an important role in facilitating the activation of CO_2 and CH_3OH molecules [90]. The effects of Cu–Ni/VSO catalyst in synthesis of DMC from CO_2 and CH_3OH have also been studied by Wu et al. [91]. They observed that the catalysts crystallinity was influenced by the reduction process and the increase in the crystallinity could enhance the DMC yield. A novel synthesized nanocomposite graphite supported Cu–Ni bimetallic catalyst has been reported to have high activity, selectivity and stability towards DMC synthesis [77]. High catalytic activity of Cu–Ni/graphite was significant because of the unique structure of graphite, moderate Cu–Ni–graphite interactions, and synergetic effects of metal Cu, Ni and Cu–Ni alloy on the CH_3OH and CO_2 activation. The reaction mechanism for the production of DMC from CH_3OH and CO_2 over novel Cu–Ni/graphite nanocomposite catalyst has also been discussed in the literature [77].

Poor mechanical stability, limited thermal stability, and low surface area of SiO_2, Al_2O_3, ZrO_2 and TiO_2 as supports have led Fan

et al. [92] to design a catalyst based-mesoporous silica for synthesis of DMC. Mesoporous silica is suitable as a catalyst support because of large surface areas, high thermal stability, well-defined uniform mesopores, and surface modification behavior. Immobilization of organotin compound of $(MeO)_2ClSi(CH_2)_3SnCl_3$ on the SBA-15 and SBA-16 mesoporous silicas was also reported by Fan et al. [92]. In their studies, four methods were used for removing the surfactants in the synthesis of mesoporous silicas: (i) calcination at 550 °C (mesocal); (ii) Soxhlet extraction with a solution of HCl in ethanol (MesoHCl-EtOH); (iii) Soxhlet extraction with a solution of pyridine (Py) in ethanol (MesoPy-EtOH) and (iv) refluxed in H_2O_2 aqueous solution (MesoH_2O_2), where Meso was referred to as mesoporous silicas. The surfactants removing methods influenced the surface area, –OH groups surface concentration, grafted organotin compound amount and catalyst activity. The catalysts activity for direct synthesis of DMC from CO_2 and CH_3OH was in the order of Sn/SBA-$15_{HCl\text{-}EtOH}$ > Sn/SBA-$15_{Py\text{-}EtOH}$ > Sn/SBA-15_{cal} > Sn/SBA-15_{H2O2}. However, the concrete reason on how the preparation methods could affect the catalyst performance has not been clearly explained in the paper.

Cai et al. [93] studied the use of K_2CO_3, KOH and CH_3OK basic catalyst with the emphasis on thermodynamics. The limited temperature and pressure conditions can only favor the reaction; thus, a new method of subroutine nesting of coupling reaction over those catalysts is required to meet the appropriate conditions and subsequently to increase the yield of DMC [93]. The effect of V-doped activated carbon (AC) supported Cu–Ni bimetal catalysts has been investigated by Bian et al. [89]. The addition of 3 wt% of V element on the Cu–Ni/AC could enhance the CH_3OH conversion by 1.2 times than the respective Cu–Ni/AC due to the uniform particle size (10–30 nm), well dispersed active metals on activated carbon surface (AC), and new phases formation between the Cu–Ni and V promoter [89]. A novel method of photo-assistant synthetic process used in preparation of copper modified (Ni, V, O) semiconductor complex catalysts has been done by Wang et al. [94]. The presence of UV light and irradiation during the catalytic reaction could reduce the reaction pressure to 0.1 MPa and enhance the activity with the increase of DMC yield up to 63%. The existence of UV irradiation or photocatalysis for reaction was more effective due to the presence of extra energy, which assisted the C–O bond cleavage of the $\cdot CO_2^-$ anion radical [94].

The use of carbon nanotubes (CNTs) as a catalyst support has been exploited due to high surface area, high capacity of hydrogen uptake and superior electronic conductivity compared to graphite and activated carbon [83]. An effective and novel catalyst utilizing CNTs supported Cu–Ni bimetal for direct synthesis of DMC from CO_2 and methanol has been reported by Bian et al. [83] with 4.3% of CH_3OH conversion and 85.0% of DMC selectivity obtained at the optimum reaction conditions. This was due to the synergetic effect of metal Cu and Ni alloy, the interaction between metal and MWCNTs, unique structure and character of MWCNTs, and homogeneously dispersed active metal particles on the MWCNTs surface [83]. Additionally, the Cu–Ni alloy phase was partially created during the calcination and activation step of catalyst [83]. The activity data of various heterogeneous catalysts for direct synthesis of DMC from CO_2 and methanol are presented in Table 4. Due to the reaction thermodynamics limitation, most of the catalysts have low catalytic activity despite the prolonged reaction time up to 12 h at respective reaction conditions. Most of the catalysts operating at higher reaction temperature demonstrated low yield of DMC because of the DMC decomposition. The design of appropriate catalyst is crucial for the reaction because of the methanol and CO_2 activation which occurs via the adsorption onto the catalyst.

4.2. *Synthesis of DMC from CO_2, methanol, and epoxides*

Epoxides compounds such as ethylene oxide, propylene oxide or styrene oxide can also be used for the synthesis of DMC with reaction of CO_2 and methanol [11,95]. The reaction occurs in two steps: (i) cycloaddtion of epoxides to CO_2 for formation of cyclic

Table 4
Various heterogeneous catalysts for direct synthesis of DMC from CO_2 and methanol.

Catalyst	Reaction condition				Reaction results		Ref.
	Calcination temperature (°C)	Pressure (MPa)	Temperature (°C)	Time (h)	Methanol conversion (%)	DMC yield (%)/mmol[(a)]	
Cu–Ni/graphite	600	1.2	105	3	10.13	0.91	[77]
H_3PO_4/ZrO_2	400	5	130	2	Na	0.63	[81]
CeO_2–ZrO_2	1000	Na	110	2	Na	0.7[(a)]	[82]
Cu–Ni/MWCNTs	Na	1.2	120	3	4.3	3.74	[83]
CeO_2–ZrO_2	1000	Na	110	4	Na	1.4 [(a)]	[84]
$H_3PW_{12}O_{40}/ZrO_2$	300	4	100	3.5	Na	2.8[(a)]	[85]
ZrO_2	300	5	170	12	Na	0.4[(a)]	[86]
TiO_2	300	5	170	12	Na	0.1[(a)]	[86]
CeO_2	300	5	170	12	Na	0.3[(a)]	[86]
$H_3PW_{12}O_{40}/ZrO_2$	300	5	170	12	Na	3.6[(a)]	[86]
$Ce_{0.1}Ti_{0.9}O2$	300	5	170	12	Na	1[(a)]	[86]
$H_3PW_{12}O_{40}/Ce_{0.1}Ti_{0.9}O_2$	300	5	170	12	Na	5[(a)]	[86]
Cu–Ni/AC	500	1.2	110	3	6.44	5.62	[89]
V–Cu–Ni/AC	500	1.2	110	3	7.76	6.98	[89]
Ni–Cu/MoSiO	450	0.1	140	Na	16.37	14.16	[90]
Ni–Cu/VSiO	450	0.1	140	Na	14.54	12.77	[90]
Cu–Ni/VSO	450	0.6	140	Na	Na	6[(a)]	[91]
Sn/SBA-15_{cal}	Na	18.2	180	10	Na	0.22	[92]
Sn/SBA-$15_{HCl\text{-}EtOH}$	Na	18.2	180	10	Na	0.41	[92]
Sn/SBA-15_{H2O2}	Na	18.2	180	10	Na	0.01	[92]
Sn/SBA-$15_{Py\text{-}EtOH}$	Na	18.2	180	10	Na	0.34	[92]
Sn/SBA-$16_{HCl\text{-}EtOH}$	Na	18.2	180	10	Na	0.22	[92]
K_2CO_3	Na	7.3	80	6	Na	4.1	[93]
KOH	Na	2.0	80	6	Na	8.5	[93]
CH_3OK	Na	2.0	80	6	Na	14.1	[93]
Cu (Ni, V, O) semiconductor	450	0.1	130	Na	4.04	6.5	[94]

[(a)]DMC yield in mmol.

carbonate (ii) transesterification of cyclic carbonate with methanol to DMC and glycol (Fig. 5). The study on various basic metal oxides catalysts has been done by Bhanage et al. [95]. Among metal oxides catalysts, MgO was effective for both reactions due to the large numbers of basic sites. Both strongly and moderately basic sites were efficiently active for the epoxides and CO_2 reaction. Moderately basic sites are required for subsequent cyclic carbonates and methanol reaction to produce DMC [95]. The catalytic performance of KOH supported on various solid base catalysts for synthesis of DMC via the reaction has been evaluated by Li et al. [96]. Among these catalysts, KOH supported on 4A molecular sieve exhibited the highest activity and could be recycled up to eight times. Under the optimized condition, propylene oxide was converted completely and gave up to 16.8% yield of DMC. They also concluded that the methanol acts as raw material and promoter for synthesis of DMC due to the increase of propylene carbonate yield when methanol was introduced in the reaction systems. High pressure CO_2 as the reaction medium in synthesis of DMC from ethylene carbonate (EC) and methanol over the K_2CO_3 catalyst has been investigated by Cui et al. [97]. Although the DMC selectivity could be enhanced about two times by pressurizing the reaction with supercritical CO_2, the ethylene carbonate conversion was still decreased due to the high pressure CO_2 which makes the ethylene carbonate compound stable and could inhibit the formation of by-products and undesired reactions [97].

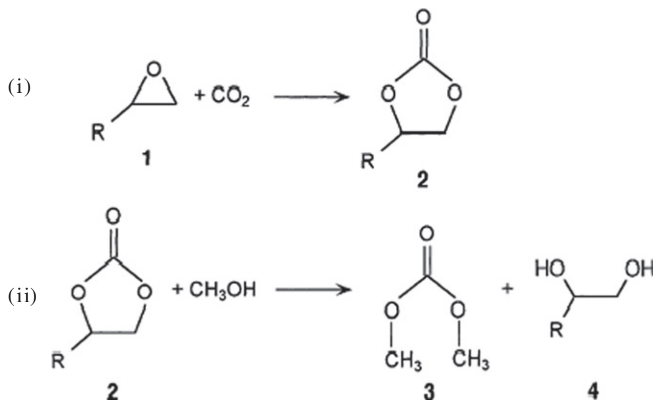


Fig. 5. Reaction step for synthesis of DMC: (i) Cycloaddition of CO_2 to epoxides; (ii) Transesterification of methanol with cyclic carbonate: 1: epoxides; 2: cyclic carbonate; 3: DMC; 4: glycol [11,95].

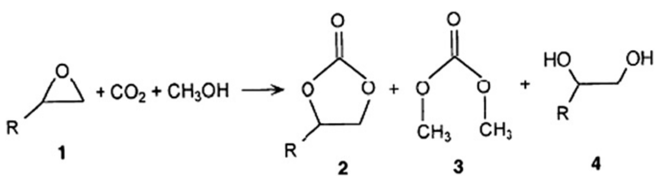


Fig. 6. One-pot synthesis of DMC from CO_2, methanol, and epoxides. 1: epoxides; 2: cyclic carbonate; 3: DMC; 4: glycol [11,95].

This reaction requires high energy consumption and high investment and production costs, due to the separation of intermediate cyclic carbonates [11]. A new method has been developed for one-pot synthesis of DMC from CO_2, methanol and epoxides as shown in Fig. 6 [11,95]. There are some works reported on one-pot system in synthesis of DMC; however, the formation of major by-products such as 1-methoxy-2-propanol and 2-methoxy-1-propanol are quite problematic for the reaction. Chen et al. [98] applied this reaction system over the [bmim]BF_4/CH_3ONa. The combination of optimum amount of [bmim]BF_4 ionic liquid and CH_3ONa showed good catalytic activity with 67.6% of DMC yield, which was higher than other similar reaction systems due to the synergetic effect between the two components and ionic liquids properties itself which acted as acid or base catalyst and a suitable reaction medium [98]. Chang et al. [99] observed that KI/ZnO and K_2CO_3–KI/ZnO catalysts were

Table 5
Various heterogeneous catalysts for synthesis of DMC from CO_2, methanol, and epoxides.

Catalyst	Reaction condition			Reaction results			Ref
	Pressure (MPa)	Temperature (°C)	Time (h)	Epoxide conversion (%)	Cyclic carbonate conversion (%)	DMC yield (%)	
MgO	8	150	4	81.9[a]	66.1	66.1	[95]
MgO	8	150	4	34.9[b]	28.0	28.0	[95]
MgO	8	150	4	92.3[c]	66.4	14.9	[95]
CaO	8	150	4	9.9[b]	25.6	25.6	[95]
ZnO	8	150	4	9.4[b]	23.0	23.0	[95]
ZrO_2	8	150	4	21.5[b]	11.8	11.8	[95]
La_2O_3	8	150	4	72.6[b]	7.1	7.1	[95]
CeO_2	8	150	4	22.7[b]	32.8	32.4	[95]
Al_2O_3	8	150	4	100[b]	4.2	4.2	[95]
K_2CO_3	8	150	4	11.3[b]	61.6	40.4	[95]
KOH/4A molecular sieve	3	180	6	100[b]	58[b]	16.8	[96]
KOH/Al_2O_3	3	180	6	Na	49[b]	13.0	[96]
KOH/Hβ	3	180	6	Na	52[b]	13.0	[96]
KOH/X	3	180	6	Na	52[b]	15.0	[96]
K_2CO_3	5.5	140	1.5	Na	47.9[a]	47.0	[97]
[bmim]BF_4/CH_3ONa	4	150	5	95.0[b]	Na	67.6	[98]
KI/ZnO	16.5	150	4	98.6[a]	Na	57.9	[99]
KI/ZnO	16.5	150	4	99.6[b]	Na	36.8	[99]
K_2CO_3–KI/ZnO	16.5	150	4	98.0[a]	Na	63.2	[99]
K_2CO_3–KI/ZnO	16.5	150	4	98.7[b]	Na	43.4	[99]
KI/MgO	16.5	150	4	96.7[a]	Na	43.8	[99]
KI/MgO	16.5	150	4	98.7[b]	na	25.8	[99]
KI/CaO	16.5	150	4	97.4[a]	Na	36.1	[99]
KI/CaO	16.5	150	4	98.9[b]	Na	17.2	[99]

[a] Ethylene carbonate.
[b] Propylene carbonate.
[c] Styrene carbonate.

Table 6
Various heterogeneous catalysts in synthesis of DMC from CO_2 and acetal or ortho-ester.

Catalyst	Co-catalyst	Acetal/ortho-ester	Reaction condition			Reaction results	Ref.
			Pressure (MPa)	Temperature (°C)	Time (h)	DMC yield (%)	
$Bu_2Sn(OMe)_2$	Na	2,2-dimethoxypropane	30	180	24	14	[100]
Polymer-supported iodide	Na	Trimethylorthoesters	200	150	6	90	[101]
Bu_2SnO	Na	2,2-dimethoxypropane	30	180	24	17	[102]
Bu_2SnO	$CH_3–C_6H_4–SO_3H$	2,2-dimethoxypropane	30	180	24	20	[102]
Bu_2SnO	$[Ph_2NH_2]\cdot OTf$	2,2-dimethoxypropane	30	180	24	40	[102]
Bu_2SnO	$[C_6F_5NH_3]\cdot OTf$	2,2-dimethoxypropane	30	180	24	40	[102]
$Ti(O\text{-}i\text{-}Pr)_4$	Na	2,2-dimethoxypropane	30	180	24	5	[102]
$Ti(O\text{-}i\text{-}Pr)_4$	$[Ph_2NH_2]\cdot OTf$	2,2-dimethoxypropane	30	180	24	25	[102]

highly active and selective for synthesis of DMC after calcinations. Complete conversion of epoxides with less than 0.2% of by-products was achieved with K_2CO_3–KI/ZnO and the catalyst could be reused four times due to the presence of stronger basic sites on the surface of K_2CO_3–KI/ZnO that makes the catalyst favorable in enhancing the activity. These researchers also reported on the activity of KI supported on CaO, MgO and ZnO. The catalytic performance of catalysts was in the order of KI/ZnO > KI/MgO > KI/CaO, while the basic sites strength of supports followed in the order of CaO > MgO > ZnO [99]. The possible reaction mechanism was also proposed in their study [99]. Table 5 presents various heterogeneous catalysts for the synthesis of DMC from CO_2, methanol, and epoxides. Although this route is possible for the synthesis of DMC, good results were not obtained because of the alcoholysis of the epoxide that influenced the formation of DMC. It was difficult to design the effective catalyst with both strong and moderate basic sites to catalyze the reaction to form DMC.

4.3. Synthesis of DMC from CO_2, acetals or ortho-ester

There are few reports on the heterogeneous catalysts in the synthesis of DMC from CO_2 and acetal or ortho-ester. Acetal or ortho-ester when used as starting materials can act as dehydrated derivative, which can avoid the negative effect and deactivation of catalysts by water in the reaction system [11,100–102]. The effective catalyst of polymer-supported iodide for such a reaction system in the presence of trimethyl orthoesters was reported by Chu et al. [101]. Sakakura et al. [100] reported that the addition of 2,2-dimethoxypropane in the reaction system could overcome the thermodynamic limitation, which showed a stable increase of DMC yield in long reaction time up to 100 h. They observed that increasing the CO_2 pressure up to 200 MPa could enhance the DMC yield and selectivity up to 90% and 100%, respectively due to the increase of CO_2 density at high pressures [100]. The addition of small amount of acidic co-catalysts to Bu_2SnO or $Ti(O\text{-}i\text{-}Pr)_4$ catalysts which led to acceleration of the yield of DMC was investigated by Choi et al. [102]. The obtained DMC yield was only 17% over Bu_2SnO without acidic co-catalysts, while the addition of *p*-toluene sulfonic acid could increase the DMC yield up to 20%. The yield of DMC increased twofold in the presence of ammonium triflates such as $[Ph_2NH_2]$OTf and $[C_6F_5NH_3]$OTf. Moreover, the addition of conventional Brönsted acid co-catalysts (HCl, H_2SO_4 and H_3PO_4) and ammonium chloride co-catalyst ((Ph_2NH_2)Cl and Bu_4NCl) in the reaction system has no significant effect in the DMC yield. Efficiency of $[Ph_2NH_2]$.OTf as co-catalyst for the $Ti(O\text{-}i\text{-}Pr)_4$ was proved by the results show five times higher DMC yield as compared to $Ti(O\text{-}i\text{-}Pr)_4$ [102]. The high catalytic activities could be related to the affinity to CO_2 and relatively strong acidities of co-catalysts [102]. It should be noted that the reaction depends strongly on the CO_2 pressure and needs to be operated at very high pressures up to 200 Mpa to obtain the optimum yield of DMC. Table 6 summarized various heterogeneous catalysts in synthesis of DMC from CO_2 and acetal or ortho-ester.

5. Conclusion

The current global warming phenomenon has led to the development of heterogeneous catalysts for the utilization of CO_2 to valuable products such as methanol, cyclic carbonate and DMC. Attention has been directed on the design of active catalysts for CO_2 conversion by combining the properties of both homo- and heterogeneous catalysts. Successful performance of Cu/ZnO-based catalysts, ionic liquid-based catalysts, and metal oxides-based catalysts for CO_2 utilization has been reported in this review; nevertheless, the CO_2 conversion and products yield are still very low and need to be operated under high reaction temperature and pressure. The addition of metal precursor, ionic liquids and either methanol, epoxides, acetal or ortho-ester in the catalytic system is reported to be effective for the production of methanol, cyclic carbonate and DMC, due to the high metal dispersion, synergistic effect between the supports and ionic liquid salts, and the starting materials in activated CO_2 molecules. There is a need for further investigations in terms of fundamental, technology, and optimization of CO_2 catalysts and reactor design in reducing global atmospheric CO_2 concentration.

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